526 Rec'd PCT/PTO 24 NOV 2000

FORM PTO-1390 (Modified) (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 200062US0XPCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): 09/700704

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP99/02745	25 MAY 1999	26 MAY 1998

TITLE OF INVENTION
CLEANING SOLUTION AND CLEANING METHOD FOR COMPONENT OF SEMICONDUCTOR PROCESSING APPARATUS

APPLICANT(S) FOR DO/EO/US
Kenichi HIROTA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
    A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report
Notice of Priority
Drawings (1 Sheet)
Amended Sheets (Pages 24, 25 and 25-1)

PCTUS1/REV03

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/700704	PCT/JP99/02745	200062US0XPCT

20. The following fees are submitted:		CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :			
☒ Search Report has been prepared by the EPO or JPO	$860.00		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482)	$690.00		
☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	$710.00		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO	$1000.00		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	$100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =		$860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).		**$0.00**	

CLAIMS	NUMBER FILED		NUMBER EXTRA		RATE		
Total claims	15	- 20 =	0	x	$18.00		
Independent claims	2	- 3 =	0	x	$80.00		
Multiple Dependent Claims (check if applicable).				☒		$270.00	
TOTAL OF ABOVE CALCULATIONS					=	$1,130.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				☐		**$0.00**	
SUBTOTAL					=	$1,130.00	
Processing fee of $130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).					+	**$0.00**	
TOTAL NATIONAL FEE					=	$1,130.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				☒		$40.00	
TOTAL FEES ENCLOSED					=	$1,170.00	
						Amount to be: refunded	$
						charged	$

☒ A check in the amount of $1,170.00 to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. in the amount of to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

22850

WILLIAM E. BEAUMONT
REGISTRATION NUMBER 30,996

SIGNATURE

Norman F. Oblon
NAME

24,618
REGISTRATION NUMBER

November 24, 2000
DATE

DESCRIPTION

CLEANING SOLUTION AND CLEANING METHOD FOR COMPONENT OF SEMICONDUCTOR PROCESSING APPARATUS

Technical Field

The present invention relates to a cleaning solution and a cleaning method for a component of a semiconductor processing apparatus. More specifically, the present invention relates to a cleaning solution and a cleaning method for removing a byproduct deposited on a component of a semiconductor processing apparatus and derived from the decomposed substances of a process gas containing C and F. Semiconductor processing here means a variety of processes executed to manufacture semiconductor devices on target substrates, such as semiconductor wafers or LCD substrates, and structures including interconnections and electrodes connected to semiconductor devices by forming semiconductor layers, insulating layers, conductive layers, and the like in predetermined patterns on the target substrates.

Background Art

Etching is one of the main semiconductor processes. Etching is performed using an etching apparatus having a process chamber in which an upper electrode is arranged to oppose a lower electrode (susceptor). To etch a silicon oxide (SiO_2) film on

the surface of a semiconductor wafer in this etching apparatus, a wafer serving as the target substrate is placed on the lower electrode. In this state, RF power is supplied to the lower electrode while a fluorocarbon-based (including a hydrofluorocarbons-based) process gas, i.e., CF-based process gas, such as CF_4, is introduced into a process chamber. With this operation, the process gas is converted into a plasma, and the silicon oxide film is anisotropically etched by this plasma.

In this etching, characteristics, such as etching anisotropy and etching rate, are controlled using the CF-based deposit produced from the decomposed substances of the process gas. More specifically, the chemical and physical actions given to the silicon oxide film from the active species and ions from the plasma are controlled by the CF-based deposit on a portion to be etched, e.g., the inner surface of a contact hole. That is, CF-based products are essential in the etching process, and CF-based byproducts also deposit on various components in the process chamber.

For example, some etching apparatus of this type includes a clamp ring for fixing a target substrate, e.g., a semiconductor wafer, on a lower electrode and a focus ring for causing a plasma produced in the process chamber to impinge on the wafer in a desired state. A baffle plate is disposed around the lower

electrode to adjust the conductance in the process chamber. A wall protecting member is disposed along the side wall in order to protect the inner surface of the process chamber. The above-mentioned CF-based byproducts cumulatively deposit on all these components.

A deposit made of a CF-based byproduct peels off when it reaches a certain thickness, thereby producing particles. This degrades the yield of semiconductor devices. For this reason, before the deposit peels off, these components must be cleaned to remove the deposit. To reduce the downtime of the apparatus, components on which a CF-based byproduct readily deposits are generally built from components that are easy to exchange. Components with a CF-based byproduct deposited thereon, after use for a predetermined period of time, are removed from the process chambers, and new cleaned equivalent components are attached to the corresponding positions.

Conventionally, components with a deposit of a CF-based byproduct attached thereto are removed and dipped in a fluorine-based solvent (e.g., perfluorocarbon: PFC) or acetone in order to swell the deposit. Then, to peel the deposit off, the components are ultrasonically vibrated in pure water and thus cleaned.

In the above cleaning, since the CF-based byproduct is removed by swelling and peeling the

deposit, a very large number of fine CF-based byproduct particles remain on the components on the microscopic level even after they are cleaned. The fine CF-based byproduct particles are peeled off by RF discharge and deposit on the wafer in the form of particles.

In etching of this type, so-called seasoning for processing a number of dummy wafers (20 to 25 dummy wafers) is generally performed after the cleaned components are mounted in the process chamber. This seasoning amounts to coating the fine residue remaining on the components with a new CF-based byproduct, thereby suppressing generation of particles below a prescribed value. The time (1 to 2 hours) for processing the dummy wafers substantially accounts for downtime of the apparatus.

The use of PFC or acetone requires several days to clean the components with the deposit made of a CF-based deposit attached thereto. This results in very low work efficiency. In addition, PFC has a global warming coefficient much larger than CO_2, although PFC is chemically stable and easy to handle. Acetone is a material toxic to man and having a low flash point. Acetone therefore requires sophisticated settings for use environment and much cost in storage and management.

Disclosure of Invention

The present invention has been made in

consideration of the conventional problems described above, and an object thereof is to provide a cleaning solution and a cleaning method for a component of a semiconductor processing apparatus, in which a CF-based byproduct can be efficiently and reliably removed.

Another object of the present invention is to provide a cleaning solution and a cleaning method for a component of a semiconductor processing apparatus, which are highly safe and hardly cause destruction of terrestrial environment.

According to the first aspect of the present invention, there is provided a cleaning solution for removing a byproduct derived from a decomposed substance of a process gas containing C and F, and deposited on a component in a process chamber of a semiconductor processing apparatus for subjecting a target substrate to a semiconductor process with the process gas, the cleaning solution containing N-methyl-2-pyrrolidone, ethylene glycol monobutyl ether, and a surfactant.

According to the second aspect of the present invention, in the cleaning solution of the first aspect, an alkali metal content is less than 10 ppb.

According to the third aspect of the present invention, the cleaning solution of the first or second aspect further contains water.

According to the fourth aspect of the present

invention, in the cleaning solution of the third aspect, the water is contained at a content of 5 to 20 wt%.

According to the fifth aspect of the present invention, in the cleaning solution according to any one of the first to fourth aspects, the surfactant is contained at a content of 0.1 to 1.0 wt%.

According to the sixth aspect of the present invention, in the cleaning solution according to the fifth aspect, the surfactant contains fluorine.

According to the seventh aspect of the present invention, in the cleaning solution according to any one of the first to sixth aspects, a total content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 80 to 90 wt%, and a ratio of a content of the N-methyl-2-pyrrolidone to the total content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 0.75 to 0.95.

According to the eighth aspect of the present invention, there is provided a cleaning method for removing a byproduct derived from a decomposed substance of a process gas containing C and F, and deposited on a component in a process chamber of a semiconductor processing apparatus for subjecting a target substrate to a semiconductor process with the process gas, the method comprising the steps of: removing the component from the process chamber; and

dipping the component in a bath of the cleaning solution according to any one of the first to seventh aspects.

According to the ninth aspect of the present invention, in the cleaning method according to the eighth aspect, the component is dipped in the bath of the cleaning solution while the component is stored in a cage with 500 to 100 meshes.

According to 10th aspect of the present invention, in the cleaning method according to the eighth or ninth aspect, the component is dipped in the bath of the cleaning solution while a temperature of the cleaning solution is set at 50 to 80℃.

According to the 11th aspect of the present invention, in the cleaning method according to any one of the eighth to 10th aspects, the semiconductor process comprises etching a layer consisting essentially of a silicon oxide on the target substrate by using the process gas.

Brief Description of Drawings

FIG. 1 is a sectional view showing a semiconductor processing apparatus according to an embodiment of the present invention;

FIG. 2 is a graph showing the experimental results about the surface tension of a cleaning solution according to the present invention; and

FIG. 3 is a view showing a state in which

a component with a deposit made of a CF-based byproduct attached thereto is dipped in a cleaning solution.

Best Mode for Carrying Out the Invention

The present inventors made extensive studies by many experiments about optimal cleaning agents for removing CF-based (e.g., fluorocarbon-based) deposits on a component of a semiconductor processing apparatus in the process of developing the present invention. As a result, the present inventors obtained the following findings.

A CF-based byproduct produced in an apparatus for etching a silicon oxide film with a CF-based gas is assumed to have a molecular structure almost the same as that of a fluorocarbon resin. The fluorocarbon resin is supposed to be very stable in high and low temperatures, chemically inactive, and not to be changed by a solvent, such as alcohol, ketone, or ester.

However, in some experiment, a component with a CF-based byproduct deposited thereon, after it was used in a process chamber of an etching apparatus of this type, was cleaned with a solution mixture (mainly containing N-methyl-2-pyrrolidone (to be also referred to as NMP hereinafter)) of NMP and ethylene glycol monobutyl ether (also called 2-butoxyethanol or butyl cellosolve), and it was found that the CF-based byproduct on the component was dissolved.

N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether are known well as solvents which dissolve a variety of synthetic resin materials well and are used in a variety of fields. These solvents are also known well as solvents which do not dissolve fluorocarbon resins.

Since the CF-based byproduct produced in the etching apparatus of this type is similar to fluorocarbon resins, as described above, the above phenomenon seemed to be contradictory to this knowledge. To confirm whether this dissolving phenomenon can be generalized, experiments were made on CF-based byproducts produced under various conditions in an etching apparatus of this type. As a result, it was confirmed that all the CF-based byproducts were dissolved in a solution mixture of NMP and 2-butoxyethanol at a given mixing ratio. Also, when a fluorocarbon resin component with the CF-based byproduct deposited thereon was dipped in a solution mixture of NMP and 2-butoxyethanol, only the CF-based byproduct was properly dissolved and removed, and the fluorocarbon resin component was substantially not damaged.

A mechanism for allowing the CF-based byproduct, which is assumed to have a molecular structure almost the same as that of fluorocarbon resins, to dissolve in the solution mixture of NMP and 2-butoxyethanol is not

clear. One possible reason is that a CF-based layer deposited as the byproduct has a molecular structure considerably different from an ideal state. In any case, the studies of the present inventors open a new path, which has never been opened by the conventional knowledge, for a cleaning solution for removing a CF-based byproduct deposited on a component of a semiconductor processing apparatus.

According to the present invention, a cleaning solution is prepared on the basis of the above findings, and is used for removing a byproduct derived from a decomposed substance of a process gas containing C and F, and deposited on the component in a process chamber of a semiconductor processing apparatus for subjecting a target substrate to a semiconductor process with the process gas. The cleaning solution contains N-methyl-2-pyrrolidone (i.e., NMP), ethylene glycol monobutyl ether (i.e., 2-butoxyethanol or butyl cellosolve), and a surfactant.

The content of an alkali metal in the cleaning solution is preferably set to be less than 10 ppb. This can prevent the alkali metal from attaching to the component of the semiconductor processing apparatus during cleaning and can also prevent a target substrate, such as a semiconductor wafer, from being contaminated when this component is used again in the process chamber.

The total content of NMP and 2-butoxyethanol in the cleaning solution is preferably set at 80 to 90 wt%. The weight ratio of the content of NMP to the total content of NMP and 2-butoxyethanol is preferably set at 0.75 to 0.95, more preferably to 0.8 to 0.9, and still more preferably 0.82 to 0.86. The CF-based byproducts were properly dissolved in these ranges in experiments in which the composition of the cleaning solution was variously changed, mainly using the mixing ratio of NMP and 2-butoxyethanol. Experiments were also conducted when the cleaning solution did not contain NMP or 2-butoxyethanol, and resulted in that the solubility of the CF-based byproduct was low, as compared with a solution mixture of NMP and 2-butoxyethanol,.

The surfactant serves to reduce the surface tension of a cleaning solution and make the cleaning solution readily permeate into the contaminant. A surfactant for minimizing the surface tension of NMP and 2-butoxyethanol is preferably used. In this respect, the surface tensions of NMP added with a silicon-containing surfactant SS and NMP added with a fluorine-containing surfactant SF were measured.

FIG. 2 is a graph showing the experimental results about the surface tensions. In FIG. 2, a content AW of each surfactant is plotted along the abscissa while the surface tension ST is plotted along the ordinate.

A broken line L1 represents a case wherein the silicon-containing surfactant is added, while a solid line L2 represents a case wherein the fluorine-containing surfactant is added. As shown in FIG. 2, according to the experiment, obviously, the surfactant to be added to the cleaning solution preferably contains fluorine, from the viewpoint of reducing the surface tension of the cleaning solution.

The content of the surfactant in the cleaning solution is preferably set at 0.1 to 1.0 wt%. As shown in FIG. 2, when the content of the surfactant is 0.1 wt% or more, the effect of reducing the surface tension of the cleaning solution can be obtained, while the surface tension is not much reduced with an increase in the content. If the content of the surfactant exceeds 1 wt%, dot-like "stains" remain on a substrate after cleaning. Since the surfactant is expensive, its content is preferably as low as possible in order to also reduce the cost of the cleaning solution.

Preferably, the cleaning solution further contains water. In this case, the water content in the cleaning solution is preferably set at 5 to 20 wt%. Since NMP and 2-butoxyethanol have flash points, water added to the cleaning solution can eliminate the flash points. The cleaning solution can then be handled as a "nondangerous article" and facilitate storage and

management. If the water content is less than 5 wt%, the cleaning solution still have a flash point. If the water content exceeds 20 wt%, the solubility of CF-based byproducts decreases.

Water in the cleaning solution also has an action of absorbing inorganic salts, such as an alkali metal, which serve as an impurity to the target substrate. Refined water from which inorganic salts are removed is preferably used as water. The refined water has a lower content of inorganic salts than pure water, as shown in Table 1 below.

Table 1

Component	Al	Cr	Ni	Fe	Cu	K	Na
Refined Water	ND	ND	ND	ND	1.49	0.66	0.56
Pure Water	2.15	ND	ND	ND	1.82	2.48	8.16

(Unit: ppb, ND: below lower detection limit)

A cleaning method for a component of a semiconductor processing apparatus using such a cleaning solution will now be described.

FIG. 1 is a sectional view showing an etching apparatus 100 having components to be cleaned with a cleaning solution according to the present invention.

A process chamber 102 of the etching apparatus 100 shown in FIG. 1 is made of a conductive metal, such as Al (aluminum), to form a process space 104 in the process chamber 102. A susceptor (lower electrode) 106

for supporting a semiconductor wafer W is disposed in the process chamber 102. The susceptor 106 is fixed in the process chamber 102 through an insulating member 108. A baffle plate 110 having a number of through holes 110a and grounded is attached around the susceptor 106. A plasma is confined in the process space 104 by the susceptor 106 and baffle plate 110. A clamp ring 112 is arranged to hold the peripheral edge of the wafer W placed on the susceptor 106. A focus ring 114 for focusing an electric field on the wafer W is disposed around the wafer W. An RF power supply 116 for outputting RF power is connected to the susceptor 106.

An upper electrode 118 serving as a counterelectrode to the susceptor 106 is arranged at a position in the process chamber 102 where it faces the support surface of the susceptor 106. The upper electrode 118 is fixed to the process chamber 102 by a peripheral ring 120 arranged around the upper electrode 118 and grounded through the process chamber 102. A number of gas discharge holes 118a connected to a gas supply source (not shown) are formed in the upper electrode 118. A process gas, e.g., a gas mixture of CF_4 and Ar is introduced into the process space 104 through the gas discharge holes 118a. The atmosphere in the process space 104 is evacuated through the through holes 110a of the baffle plate 110 and the gap between

the baffle plate 110 and the inner wall surface of the process space 104. The inner side surface of the process chamber 102 is covered with a wall protecting member 122 in correspondence with the process space 104 in order to prevent the plasma from directly contacting the side wall of the process chamber 102.

The baffle plate 110, clamp ring 112, focus ring 114, peripheral ring 120, wall protecting member 122 are made of a ceramic, Al whose surface is covered with Al_2O_3, Al_2O_3, fluorocarbon resin, polyimide, or Si in accordance with their application purposes. These members are detachable singly from the process chamber 102 and interchangeable with new equivalent components.

The etching apparatus 100 is typically used to etch a silicon oxide (SiO_2) film on the surface of the semiconductor wafer W.

In etching, the wafer W is placed on the susceptor 106 and fixed with the clamp ring 112. A gas mixture of CF_4 and Ar is introduced into the process space 104 through the gas discharge holes 118a. The process chamber 104 is evacuated and kept in a predetermined reduced pressure atmosphere. A predetermined RF power is then applied to the susceptor 106 to ionize the process gas introduced into the process space 104, thereby generating a plasma. The SiO_2 film on the wafer W is then etched using this plasma. When the etching is performed for a predetermined period of

time, the wafer W is unloaded from the process chamber 102 and transferred to the next processing apparatus.

During etching, a reaction byproduct is produced in the process space 104 and attaches to a variety of components (members) arranged in the process space 104. More specifically, as in this embodiment, when the SiO_2 film on the wafer W is etched using the gas mixture of CF_4 and Ar, a CF-based byproduct attaches to the components, such as the baffle plate 110, clamp ring 112, focus ring 114, peripheral ring 120, and wall protecting member 122. The deposition amount of the CF-based byproduct on these components increases in proportion to the process time.

When thickness of the deposit made of the CF-based byproduct reaches a certain value, the deposit peels off to generate particles. These particles cause dielectric breakdown of semiconductor devices to reduce the yield of products. For this reason, before the deposit peels off, these components must be cleaned to remove the deposit. That is, components with the CF-based byproduct attached thereto upon use for a predetermined period of time are detached from the process chamber and replaced with new cleaned equivalent components.

After use for a predetermined period of time, components, such as the baffle plate 110, clamp ring 112, focus ring 114, peripheral ring 120, and wall

protecting member 122, are replaced with new equivalent components. In this case, when a series of etching operations for the wafer W are complete and the final wafer W is unloaded from the process chamber 102, the interior of the process chamber r102 is replaced with an inactive gas, and components which are required to be replaced are removed from the process chamber 102. As shown in FIG. 3, these components are dipped in a bath 12 containing a cleaning solution having the above composition according to the present invention for a predetermined period of time, e.g., 7 hours to perform chemical cleaning. Note that the focus ring 114 is exemplified as a component with a deposit made of a CF-based byproduct attached thereto in FIG. 3.

In this case, the temperature of the cleaning solution is maintained in the range of 20℃ to 80℃ and preferably 50℃ to 80℃. As a result, the cleaning solution permeates into the CF-based byproduct attached to the component 114. The CF-based byproduct is dissolved at low speed while swelling, and thus the CF-based byproduct peels off from the component 114. Fine CF-based byproducts which tend to remain on the component in chemical cleaning can be dissolved with the cleaning solution.

In chemical cleaning, as shown in FIG. 3, the component 114 is dipped in the bath 12 of the cleaning solution while being kept in a cage 14 with 500 to

100 meshes. The CF-based byproduct peeled off from the component 114 is removed together when the component 114 is removed from the bath 12. This operation is required because the cleaning solution according to the present invention dissolves the CF-based byproduct while perfluorocarbon or acetone used as the conventional cleaning solution does not dissolve the CF-based byproduct. That is, when the CF-based byproduct peeled off from the component 114 stays in the bath 12 of the cleaning solution, the byproduct gradually dissolves in the bath 12 to change the composition of the cleaning solution. In this case, the bath 12 containing the cleaning solution must be frequently replaced with a new one.

The component 114 having undergone the chemical cleaning is dipped in refined water and washed with the water. With this operation, the contaminant attached to the component 114 during the chemical cleaning can be reliably removed. The component 114 is dried and then mounted in the process chamber 102 again when the corresponding component in the process chamber 102 is required for replacement.

A comparative experiment for cleaning components with a CF-based byproduct deposited thereon was conducted using an example of the above cleaning method and a comparative example of the conventional method. The component to be cleaned was the one made of Al

having the surface covered with Al_2O_3 and was used in the etching apparatus 100 shown in FIG. 1 for a predetermined period of time generally requiring periodical replacement.

In the example of the present invention, a cleaning solution had a composition consisting of 75 wt% NMP, 15 wt% 2-butoxyethanol, 0.5 wt% surfactant, and 9.5 wt% water, the temperature of the bath 12 containing the cleaning water was 50℃, and the dipping time of the component was 7 hours. In the comparative example of the conventional method, the cleaning solution was acetone, the temperature of the bath of the cleaning solution was 15℃, and the dipping time of the component was 5 hours.

Table 2 shows changes in the numbers of particles attached to wafers, when the component was processed by the example of the present invention and was mounted in the process chamber 102 for etching. Each wafer used was a 200-mm Si wafer, and the size of each detected particle was 0.2 μm or more. In general, when the size of detected particle is set at 0.2 μm or more for a 200-mm wafer, the wafer having 30 particles or less is regarded to satisfy the standard. That is, as shown in Table 2, according to the example of the present invention, when only one dummy wafer is processed, processing of an actual wafer can be started.

Table 2

Wafer No.	1	2	3	4	5	6	7	8
No. of Particles	215	10	6	2	0	3	6	6

In contrast, according to the comparative example of the conventional method, the 20th wafer had 30 or less particles each having a size of 0.2 μm or more for the first time. That is, according to the comparative example of the conventional method, unless 20 or more dummy wafers are processed, processing of an actual wafer cannot be started. The processing of 20 dummy wafers takes 1 to 2 hours, which substantially accounts for downtime of the apparatus.

About 20 larger particles detected on the first wafer of the example of the present invention were analyzed by EDX (Energy Dispersible X-ray spectroscopy) in descending order of particle size. As a result, no CF-based particles were detected, and combinations of Al, O, and S accounted for most particles.

The cause of this can be thought as follows. That is, since a component used in the experiment is made of Al having the surface covered (anodized) with Al_2O_3, Al and O are present on the surface of the component. S is also present on the surface of the component because sulfuric acid is used in anodizing the component. Accordingly, Al, O, and S can be generated by friction when the component is mounted in

the process chamber 102. These particles are weakly attached to the surface of the component, and most of the particles are detached from the surface of the component by initial RF discharge in etching. The particles are then exhausted outside the process chamber 102. Therefore, the number of detected particles is greatly reduced from the second wafer.

In contrast, in the comparative example of the conventional method, a fine CF-based byproduct probably is attached to and remains on the component. Since the CF-based byproduct is strongly attached to the surface of the component, it cannot be peeled off at once by the RF discharge in etching. Therefore, a larger number of dummy wafers have to be processed, that is, seasoning is required.

An experiment was conducted to check the relationship between the temperature of the cleaning solution according to the present invention and the solubility of the CF-based byproduct. In this experiment, the cleaning solution had a composition consisting of 75 wt% NMP, 15 wt% 2-butoxyethanol, 0.5 wt% surfactant, and 9.5 wt% water. A component with the CF-based byproduct deposited thereon was dipped in the cleaning solution for 3 hours.

Table 3 shows the results of measuring the solubilities of the CF-based byproduct at cleaning solution temperatures of 20℃, 50℃, and 70℃. As shown

in Table 3, the higher the cleaning solution temperature, the higher the solubility. The larger the thickness of the CF-based byproduct to be removed, preferably the higher the cleaning solution temperature. However, when the temperature of the cleaning solution excessively increases, water is evaporated and the cleaning solution components undesirably exhibit flash points. From this viewpoint, the temperature of the cleaning solution is preferably set at 50 to 80℃.

Table 3

Temperature	Initial Weight (g)	Weight after Cleaning (g)	Solubility (%)
20℃	2.00	1.99	0.5
50℃	2.00	1.77	11.5
70℃	2.00	1.67	16.5

As described above, the cleaning solution according to the present invention can more efficiently and reliably remove CF-based byproducts than the conventional cleaning solution. NMP (N-methyl-2-pyrrolidone) and 2-butoxyethanol (ethylene glycol monobutyl ether) are less toxic and rarely affect human health. Since NMP and 2-butoxyethanol readily decompose in outer air, use of these materials does not become one of the causes of global warming. Since NMP is inexpensive, use of this material does not increase the cleaning cost of the components of the semiconductor processing apparatus. Examples of the material of the component to be cleaned are ceramic, Al whose

surface is covered with Al_2O_3, Al_2O_3, fluorocarbon resin, polyimide, and Si. Note that polyimide readily dissolves in the cleaning solution according to the present invention and a polyimide component must be cleaned within a short time. Semiconductor processing which generates CF-based byproducts is not only etching but also CVD.

The present invention has been described with reference to a preferred embodiment of the present invention in conjunction with the accompanying drawings. The present invention, however, is not limited to this. Various changes and modifications can be anticipated by those skilled in the art within the range of technical scope defined in the appended claims. These changes and modifications should be construed to be incorporated in the technical scope of the present invention.

C L A I M S

1. (amended) A cleaning solution for removing a byproduct derived from a decomposed substance of a process gas containing C and F, and deposited on a component in a process chamber of a semiconductor processing apparatus for subjecting a target substrate to a semiconductor process with the process gas,

the cleaning solution containing N-methyl-2-pyrrolidone, ethylene glycol monobutyl ether, and a surfactant, with an alkali metal content of less than 10 ppb.

2. (deleted).

3. (amended) The cleaning solution according to claim 1, further containing water.

4. The cleaning solution according to claim 3, wherein the water is contained at a content of 5 to 20 wt%.

5. (amended) The cleaning solution according to any one of claims 1, 3, and 4, wherein the surfactant is contained at a content of 0.1 to 1.0 wt%.

6. The cleaning solution according to claim 5, wherein the surfactant contains fluorine.

7. (amended) The cleaning solution according to any one of claims 1, 3, and 6, wherein a total content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 80 to 90 wt%, and a ratio of a content of the N-methyl-2-pyrrolidone to the total

content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 0.75 to 0.95.

8. (amended) A cleaning method for removing a byproduct derived from a decomposed substance of a process gas containing C and F, and deposited on a component in a process chamber of a semiconductor processing apparatus for subjecting a target substrate to a semiconductor process with the process gas,

the method comprising the steps of:

removing the component from the process chamber; and

dipping the component in a bath of a cleaning solution containing N-methyl-2-pyrrolidone, ethylene glycol monobutyl ether, and a surfactant.

9. The cleaning method according to claim 8, wherein the component is dipped in the bath of the cleaning solution while the component is stored in a cage with 500 to 100 meshes.

10. The cleaning method according to claim 8 or 9, wherein the component is dipped in the bath of the cleaning solution while a temperature of the cleaning solution is set at 50 to 80℃.

11. The cleaning method according to any one of claims 8 to 10, wherein the semiconductor process comprises etching a layer consisting essentially of a silicon oxide on the target substrate by using the process gas.

12. (added) The cleaning method according to any one of claims 8 to 11, wherein an alkali metal content is less than 10 ppb.

13. (added) The cleaning method according to any one of claims 8 to 12, wherein, in the cleaning solution, a total content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 80 to 90 wt%, and a ratio of a content of the N-methyl-2-pyrrolidone to the total content of the N-methyl-2-pyrrolidone and ethylene glycol monobutyl ether is 0.75 to 0.95.

A B S T R A C T

A cleaning solution is used to remove a byproduct derived from a decomposed substance of a process gas containing C and F. The cleaning solution contains 75 wt% N-methyl-2-pyrrolidone, 15 wt% ethylene glycol monobutyl ether, 0.5 wt% surfactant, and 9.5 wt% water. The content of an alkali metal in the cleaning solution is set to be less than 10 ppb.

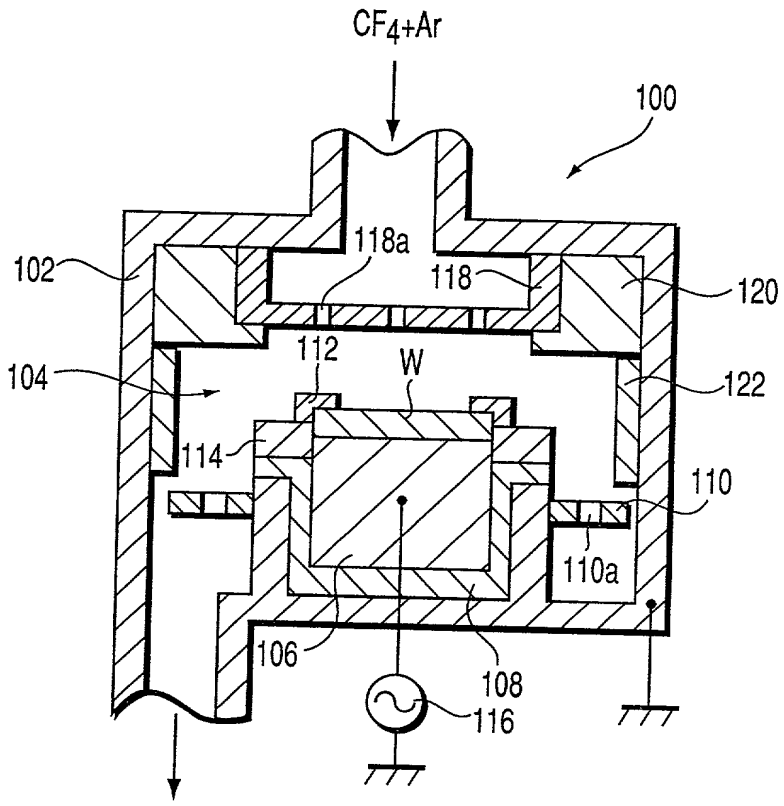

FIG. 1

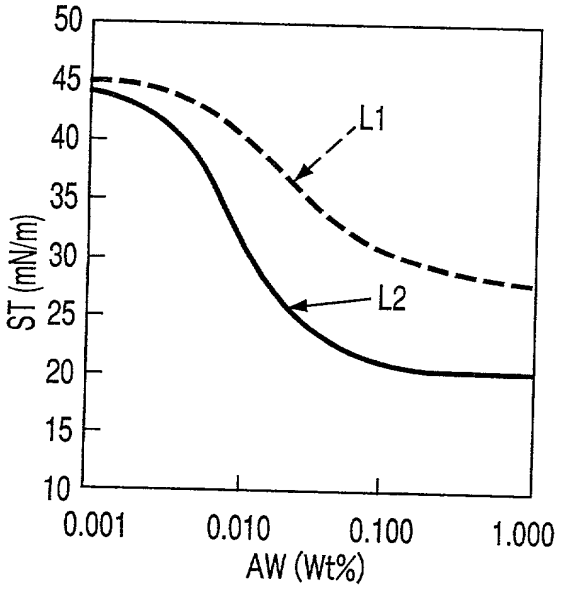

FIG. 2

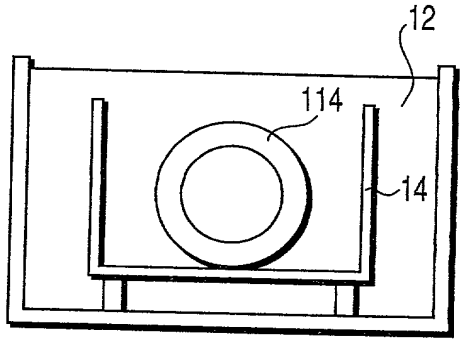

FIG. 3

Declaration Power of Attorney For Patent Application
特 許 出 願 宣 言
Japanese Language Declaration

私は、下欄に氏名を記載した発明として、以下の通り宣言する：

As a below named inventor, I hereby declare that:

私の住所、郵便の宛先および国籍は、下欄に氏名に続いて記載したとおりであり、

My residence, post office address and citizenship are as stated below next to my name,

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

半導体処理装置の部品の洗浄液及び洗浄方法

CLEANING SOLUTION AND CLEANING METHOD FOR COMPONENT OF SEMICONDUCTOR PROCESSING APPARATUS

その明細書を
（該当するほうに印を付す）

The specification of which
(check one)

☐ ここに添付する。

☒ 1999, 5 月 25 日に

☐ is attached hereto.

☒ was filed on MAY 25, 1999

as Application Serial No.

出願番号第 PCT/JP99/02745 号として

PCT/JP99/02745 and was amended on

提出し、 2000, 1 月 6 日に補正した。
（該当する場合）

January 6, 2000
(if applicable)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第３７部第１章第５６条（ａ）項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a).

Japanese Language Declaration

私は、合衆国法典第３５部第１１９条、第１７２条、又は第３６５条に基づく下記の外国特許出願又は発明者証出願の外国優先権利益を主張し、さらに優先権の主張に係わる基礎出願の出願日前の出願日を有する外国特許出願又は発明者証出願を以下に明記する：

I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119, Sec. 172 or Sec. 365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior foreign application(s)
先の外国出願

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)	Priority Claimed 優先権の主張 Yes あり	No なし
10-183230	JAPAN	26/05/1998	☒	☐
			☐	☐
			☐	☐
			☐	☐
			☐	☐

私は、合衆国法典第３５部第１２０条に基づく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第３５部第１１２条第１項に規定の態様で先の合衆国出願に開示されていない限度において、先の出願の出願日と本願の国内出願日又はＰＣＴ国際出願日の間に公表された連邦規則法典第３７部第１章第５６条（ａ）項に記載の所要の情報を開示すべき義務を有することを認める。

I hereby claim the benefit of Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112, I acknowledge the duty to disclose any material information as defined in Title 37, Code of Federal Regulations, Sec. 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)

私は、ここに自己の知識に基づいて行った陳述がすべて真実であり、自己の有する情報及び信ずるところに従って行った陳述で真実であると信じ、更に故意に虚偽の陳述等を行った場合、合衆国法典第１８部第１００１条により、罰金もしくは禁固に処せられるか、又はこれらの刑が併科され、又はかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損なうことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true; and further that all statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Japanese Language Declaration

（日本語宣言書）

委任状：私は、下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
（弁理士、または代理人の氏名及び登録番号を明記のこと）

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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(Supply similar information and signature for second and subsequent joint inventors.)

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